

Blend Membranes from Carboxymethylated Chitosan/Alginate in Aqueous Solution

LINA ZHANG,¹ JI GUO,¹ JINPING ZHOU,¹ GUANG YANG,¹ YUMIN DU²

¹ Department of Chemistry, Wuhan University, Wuhan 430072, China

² Department of Environmental Science and Engineering, Wuhan University 430072, China

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ABSTRACT: The blend membranes were satisfactorily prepared by coagulating a mixture of O-carboxymethylated chitosan (CM-chitosan) and alginate in aqueous solution with 5 wt % CaCl₂, and then by treating with 1 wt % HCl aqueous solution. Their structure and miscibility were characterized by scanning electron micrograph, X-ray diffraction, infrared spectra, differential thermal analysis, and atomic absorption spectrophotometer. The results indicated that the blends were miscible, when the weight ratio of CM-chitosan to alginate was in the range from 1 : 1 to 1 : 5. The polymers interpenetration including a Ca²⁺ crosslinked bridge occurred in the blend membrane, and leads to high separation factor for pervaporation separation of alcohol/water and low permeation. The tensile strength in the wet state ($\sigma_b = 192 \text{ kg cm}^{-2}$ for CM-chitosan/alginate 1 : 1) and thermostability of the blend membranes were significantly superior to that of alginic acid membrane, and cellulose/alginate blend membranes, owing to a strong electrostatic interaction caused by —NH₂ groups of CM-chitosan with —COOH groups of algic acid. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 610–616, 2000

Key words: carboxymethylated chitosan; alginate; blend membrane; miscibility; calcium bridge

INTRODUCTION

Nowadays, the natural polymers from marine resources such as chitin and alginate have attracted more and more attention, owing to their abundant sources, friendliness to the environment, and potential to substitute for some petrochemicals. Chitosan, a β -(1 → 4)-2-amino-2-deoxy-D-glucose, is a polyaminosaccharide derived from N-deacetylation of chitin. Due to their good biological activity, biocompatibility, and biodegrad-

ability, chitosan and its derivatives have been used as biomedical polymers.^{1,2} These biomolecules have applications as anticoagulants, wound-healing accelerators, wound dressings, artificial bone and skin, immobilization of enzyme, and elements in drug delivery systems.^{3–6}

Alginic acid is a heteropolysaccharide that consists of β -(1 → 4)-D-mannuronic acid and α -(1 → 4)-L-glucuronic acid,⁷ and the alginate membranes give an outstanding performance in the dehydration of ethanol–water mixtures.^{8,9} It was reported that alginate has a high inhibitory activity against the tobacco mosaic virus,¹⁰ and also inhibits the toxicity of terrible cadmium¹¹ and radioactive strontium.¹² The calcium alginate microcapsules have been utilized as hemoglobin carries and for macromolecular deliver.^{13,14} There-

Correspondence to: L. Zhang.

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fore, chitosan and alginate all are ideal biopolymer materials. Recently, chitosan/calcium alginate encapsulation of albumin and hirudin, the mechanical and release properties of chitosan/alginate capsules encapsulating bovine serum albumin, and the selective sorption behavior of sodium alginate membrane crosslinked with glutaraldehyde were investigated by Rao et al.,¹⁵ Chen et al.,¹⁶ and Yeom et al.,¹⁷ respectively. Understanding of the structure and mechanical properties of their blend membranes in the wet state is very important for the applications. However, published studies on chitosan/alginate blend membranes are scarce.

In our laboratory, blend membranes of cellulose cuoxam, a cuprammonium cellulose complex, with casein¹⁸ and alginate,⁷ respectively, have been satisfactorily investigated. The experimental results indicated that mechanical properties of the blend membranes in both the dry and wet states were markedly superior to that of the nonblend, owing to the interaction between the hydroxyl groups of cellulose and carboxylate groups of casein or alginate. However, preparing a blend membrane of chitosan and alginate failed, because they aggregated to a hydrogel in aqueous solution. This has prompted us to search the blend membranes from water-soluble carboxymethylated (CM) chitosan and water-soluble sodium alginate. In this work, the blend membranes were prepared by coagulating a mixture of CM-chitosan and alginate in aqueous solution, and their structure and properties were studied and discussed.

EXPERIMENTAL

Materials

The sodium alginate was purchased from Shanghai Chemical Reagent Company. Chitosan supplied by Yuhuan Ocean Biochemistry Co., Ltd., in Zhejiang province. The deacetylation degree of chitosan is 87%. Carboxymethylated chitosan was prepared according to the literature.¹⁹ The chitosan, suspend in 42 wt % NaOH aqueous solution, reacted with monochloroacetic acid at 20°C for 6 h, and then neutralized with HCl aqueous solution (pH 5). The product was washed with alcohol, then vacuum dried to give O-CM-chitosan with 1.0 of the substituting degree.¹⁹ The CM-chitosan in 0.2 mol L⁻¹ NaCl aqueous solution was measured by DAWN DSP Laser Photometer

(Wyatt Technology) equipped with SPECTRA SERIS P100 GPC, and double peaks in GPC chromatogram were observed, suggesting that single chains and aggregates²⁰ coexist in the solution. The weight-average molecular weights (M_w) of the CM-chitosan were obtained to be 1.5×10^5 for the single chain and 5.6×10^5 for its aggregate.

Preparation of Blend Membranes

The preparation methods of blend membranes were as follows: a mixture of 5 wt % CM-chitosan aqueous solution and 8 wt % sodium alginate aqueous solution was stirred for 15 min, then filtered and degassed. The blend solution was spread over a glass plate to depth of 0.2 mm and coagulated in a coagulation bath of 5 wt % CaCl₂ aqueous solution for 15 min. After washing by water, the membrane was regenerated in 1 wt % HCl aqueous solution to get transparent blend membranes of CM-chitosan/alginate, then washed with running water. The blend membrane was dried on the glass plate in air. By changing the weight ratio of CM-chitosan to alginate such as 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5, we prepared a series of blend membranes coded as CCHAL-1, CCHAL-2, CCHAL-3, CCHAL-4, and CCHAL-5. The membranes CCH and AL were prepared from pure polymer of CM-chitosan and alginate solution, respectively. Because CM-chitosan cannot form membranes under the same conditions, the membrane CCH was prepared as follows: the 5 wt % aqueous CM-chitosan solution was spread over a glass plate and dried in air at 50°C, then immersed into acetone for 30 min, finally dried in air.

Characterization

Infrared (IR) spectra of the membranes were recorded with a Nicolet 170 SX FTIR spectrometer. A scanning electron micrograph (SEM) was taken with a Hitachi S-570 SEM. The membranes were coated with gold, subsequently, their surface were observed and photographed. X-ray diffraction was measured with an X-ray diffractometer (Rigaku Dmax- γ A). The X-ray diffraction patterns with CuK α at 40 kV and 50 mA were recorded in the region of $2\theta = 5^\circ \sim 35^\circ$. The degree of crystallinity (χ_c) was calculated according to Rabek's method.²¹ The contents of calcium and sodium in the membranes were determined with a Hitachi 180-80 Polarized Zeeman atomic absorption spectrophotometer (AAS). For the determination of

these elements, the membranes were treated as follows: 0.02 g of blend membrane plus 5 mL concentrated HNO_3 were heated to about 100°C to get a carbonization product, while keeping the solution slightly boiling. After cooling, 2 mL concentrated HNO_3 was added, and the process above was repeated. After the second cooling, 1 mL concentrated HNO_3 and 1 mL concentrated HCl were added. Subsequently, the mixture was heated to get a clear solution for the AAS determination.

Differential thermal analysis (DTA) was carried out using a thermal analyzer (Shimadzu DT-40). The membrane was cut to pieces with 2 mm length (about 5 mg), then analyzed under nitrogen atmosphere from 30 to 380°C at a heat rate of $20^\circ\text{C min}^{-1}$.

Measurements of Properties

The tensile strength (σ_b) of dry and wet membranes was measured by an electronic strength tester (XLD-0.1, the Second Tensile Testing Machine Manufactory of Changchun, China) according to the Chinese standard method (GB4456-84) at a tensile rate of 100 mm min^{-1} .²² The wet membrane was measured immediately after immersing in water for 10 min. Three membranes with size of $2 \times 5 \text{ cm}^2$ were tested for every kind, and their average value was given. The water resistivity (R) of the membranes was evaluated from σ_b (dry) value in dry state and σ_b (wet) in wet state by the following equation:

$$R = \sigma_b(\text{wet})/\sigma_b(\text{dry}) \quad (1)$$

The swelling ratios (S) of membranes in water were determined by immersing a piece of membrane ($1 \times 3 \text{ cm}$) in 500 mL water for 24 h. The value of S was calculated as following:

$$S = [(W_w - W_d)/W_d] \times 100\% \quad (2)$$

where W_w is the weight of swollen membrane, g; W_d is the weight of dry membrane, g, which was dried in vacuum at room temperature for 24 h.

Pervaporation of Membranes

Pervaporation test was performed on a pervaporation apparatus made in Fudan University, according to Huang's method,⁹ except for permeation flux.²³ Permeation flux (J) of the membranes was calculated by

$$J = W/(A \times t) \quad (3)$$

where W is the weight of permeate liquid, A is the effective membrane area, and t is the operating time. The separation factor (α) for alcohol/water mixture was determined by

$$\alpha = [Y_w/Y_a]/[X_w/X_a] \quad (4)$$

where X_w , X_a are the weight fraction of water (w) and alcohol (a) in the feed solution; Y_w , Y_a are the weight fraction of water (w) and alcohol (a) in the permeated solution. The concentration of alcohol in the permeated solution was determined by gas chromatography.

RESULTS AND DISCUSSION

Miscibility of Blends

Many experimental results^{7,15-18} have indicated that the presence of special interactions in a blend including hydrogen bonding, ion-ion pairing, etc., favors the enthalpy for mixing, and allows the components to mix completely. Among the entire interaction examined, hydrogen bonding quite efficiently improves the miscibility without accompanying much change of the component polymers.²⁴ The IR spectra for the membranes CCH, AL, CCHAL-1, CCHAL-3, and CCHAL-5 are shown in Figure 1. The —OH stretching vibration bands of the blend membranes were broadened and shifted to lower wavenumber compared with CCH and AL (at 3400 cm^{-1}), suggesting that intermolecular hydrogen bonds exist in the blend membranes. The peak broadened with increasing content of CM-chitosan in the blend membrane. For CCH and AL, the absorption bands at 1610 and 1619 cm^{-1} are assigned to $\text{C}=\text{O}$ of —O—CO— CH_3 in CM-chitosan and $\text{C}=\text{O}$ of —COOH in alginic acid, respectively. However, the absorption band of the blend membranes were at around 1630 cm^{-1} , and all the blend membranes have a new absorption band at 1740 cm^{-1} caused by electrostatic interaction between —COOH groups of alginic acid and — NH_2 groups of chitosan rather than —OH of chitosan. This band does not appear in cellulose/alginic acid blend membranes.⁷ It was further proved that the substitution was not through the — NH_2 groups of CM-chitosan. With the increase of CM-chitosan content, the band intensity of blend membranes increased, and the band shifted from 1747 to 1737

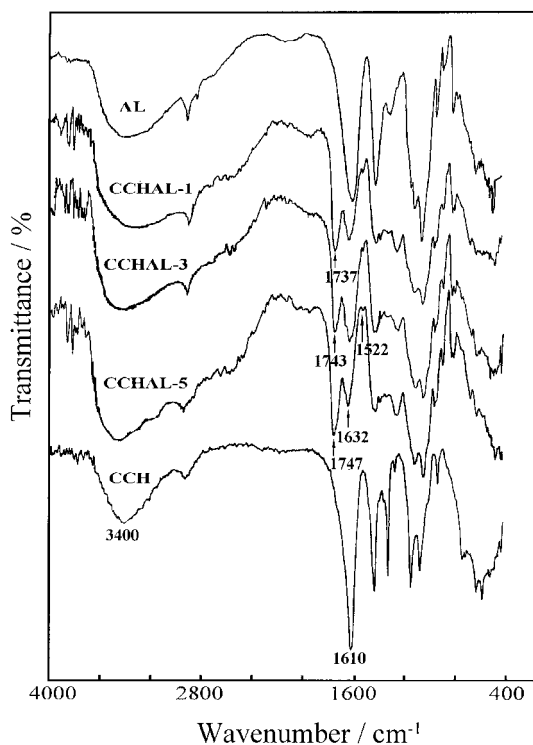


Figure 1 IR spectra of the membranes AL, CCHAL-1, CCHAL-3, CCHAL-5, and CCH.

cm^{-1} , suggesting that the electrostatic interaction between $-\text{COOH}$ groups of alginic acid and protonated $-\text{NH}_2$ groups of CM-chitosan en-

hanced. The IR results indicated that the blend between the two kinds of molecules is miscible, due to the strong electrostatic force and intermolecular hydrogen bonding.

Figure 2 shows SEM of the membranes. The blend membranes display smooth surface (B and C) similar to the blend membrane (CNAL6-1) of cellulose/alginate,⁷ indicating the miscibility between CM-chitosan and alginate.

The X-ray diffractograms of the blend membranes are described in Figure 3. The degree of crystallinity (χ_c) has the order CCHAL-1 < CCHAL-3 < CCHAL-5 < AL and gives values of 38, 41, 45, and 52, respectively. It is clear that the χ_c values of the blend membranes are lower than that of membrane of alginic acid, and decreased with increase of CM-chitosan content, suggesting the certain level of miscibility for the blend membranes.

Figure 4 shows the DTA thermograms of the membranes. The single endothermic peak in range of 190 ~ 200°C suggests that some chain scission and loss of water molecules coming from the primary $-\text{OH}$ groups of alginate in the membranes CCHAL and AL occurred.²⁵ The endothermic peaks shifted to the higher temperature with increasing content of CM-chitosan, owing to enhancement of intermolecular interaction in the blend membranes. Interestingly, an exothermic peak of the membrane CCH appears at 282°C,

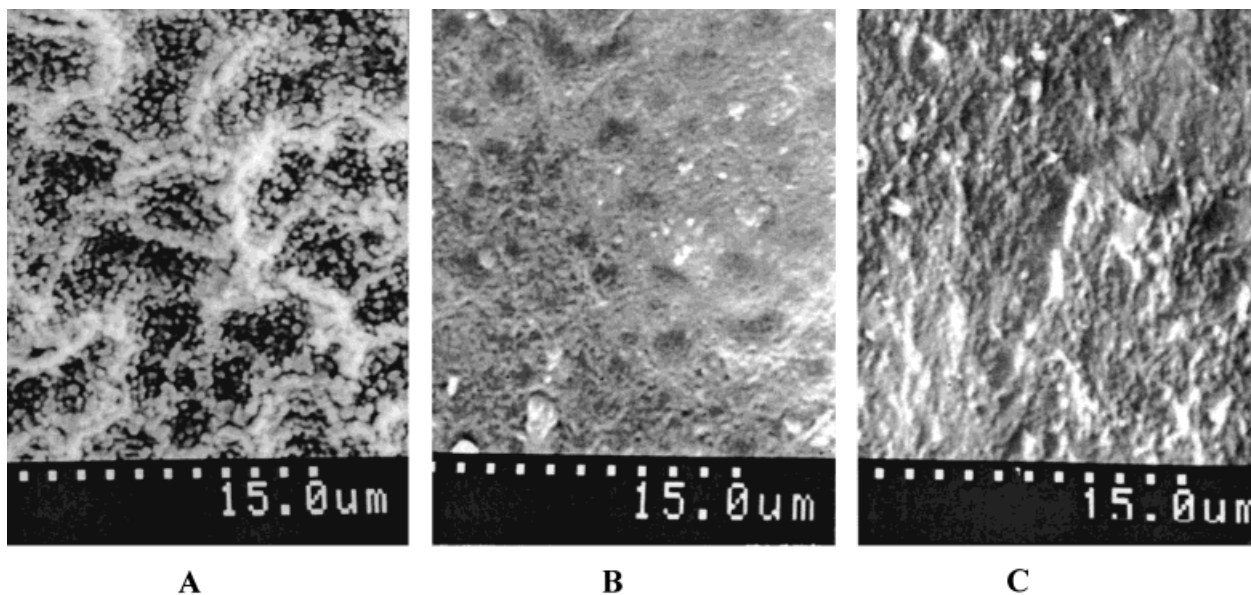


Figure 2 SEM of the membranes CCH (A), CCHAL-3 (B), and CCHAL-5 (C) for the front surface.

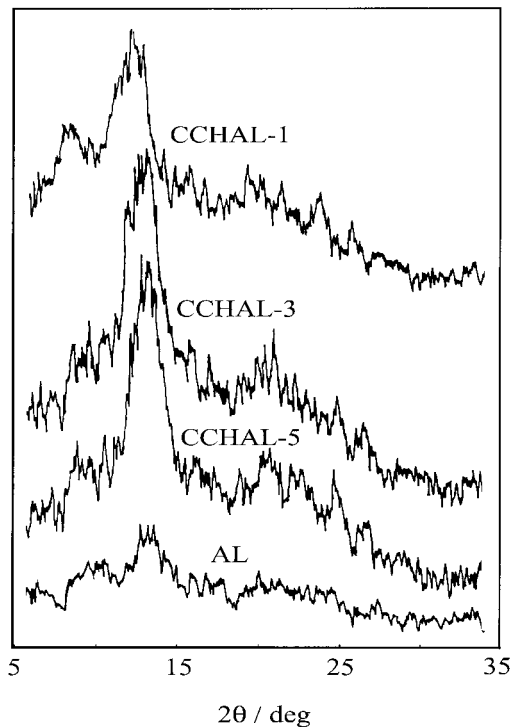


Figure 3 X-ray diffraction patterns of the membranes CCHAL-1, CCHAL-3, CCHAL-5 and AL.

owing to the decomposition of CM-chitosan,²⁶ but disappears in the blend membranes. The results support the conclusion on the miscibility of the blends.

Mechanical Properties

The effect of the weight fraction of alginate (W_{AL}) on the mechanical properties of the blend membranes in wet state is described in Figure 5. The values of tensile strength σ_b for the membranes in dry and wet states are summarized in Table I. The σ_b of wet membranes increased with increasing CM-chitosan content, and a maximum reached to be 192 kg cm^{-2} for the CCHAL-1 membrane. The AL membrane prepared by pure alginate is very weak in wet state, while tensile strength of the blend membranes is much higher than the nonblend. It is obvious that CM-chitosan plays an important role in improving mechanical properties of the blend membranes in wet state. The blend membranes have promising application as hydrophilic function-membrane in the field of medical and biological materials.

Figure 6 shows the dependence of the water resistivity (R) of the membranes on Ca^{2+} content. The water resistivities of the blend membranes

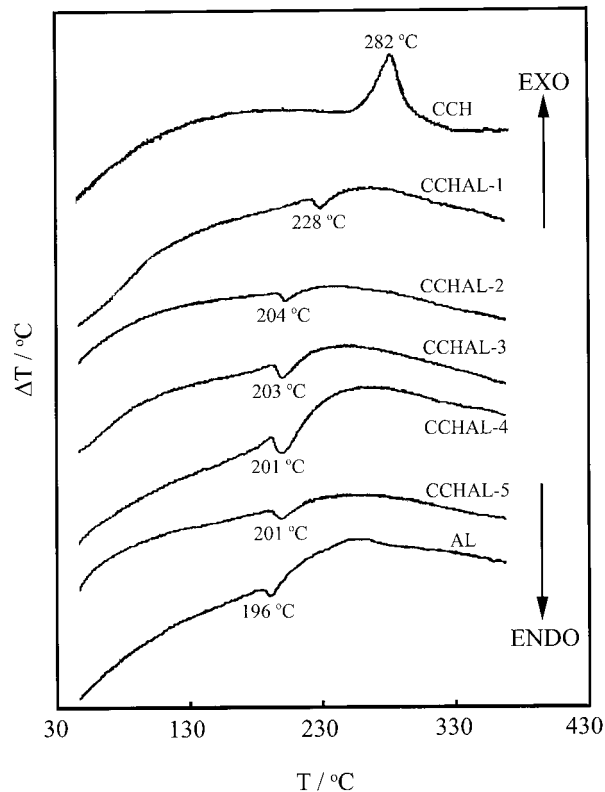


Figure 4 DTA curves of the membranes AL, CCHAL-5, CCHAL-4, CCHAL-3, CCHAL-2, CCHAL-1, and CCH.

are significantly higher than the nonblend membrane AL ($R = 0.15$) as shown in Table I. R values of blend membranes decreased with increasing Ca^{2+} content until $W_{\text{Ca}^{2+}} = 0.08 \text{ mmol mg}^{-1}$, then hardly changed. Effect of Ca^{2+} content on swelling ration (S) of membranes is shown in Figure 7. Interestingly, the swelling ration of the blend

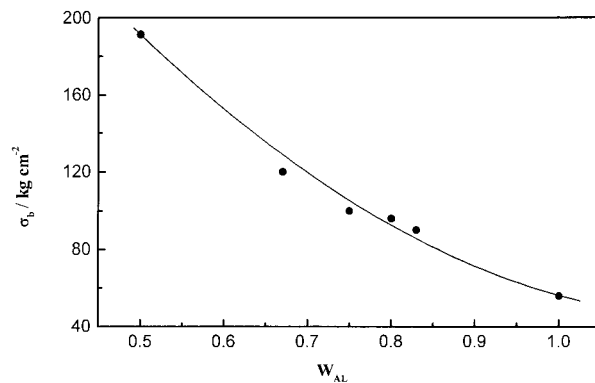


Figure 5 Dependence of tensile strength (σ_b) of wet membranes on alginate content (W_{AL}) in the blend membrane.

Table I Element Content and Mechanical Properties of the Membranes

| Membrane | Ca (mmol g ⁻¹) | Na (mmol g ⁻¹) | σ_b (kg cm ⁻²) | | <i>R</i> | <i>S</i> (%) |
|----------|----------------------------|----------------------------|-----------------------------------|-----|----------|--------------|
| | | | Dry | Wet | | |
| AL | 0.24 | 0.06 | 410 | 60 | 0.15 | — |
| CCHAL-1 | 0.04 | 0.04 | 404 | 192 | 0.48 | 173 |
| CCHAL-2 | 0.06 | 0.01 | 276 | 120 | 0.44 | 238 |
| CCHAL-3 | 0.18 | 0.06 | 480 | 100 | 0.21 | 204 |
| CCHAL-4 | 0.08 | 0.05 | 383 | 96 | 0.25 | 250 |
| CCHAL-5 | 0.05 | 0.05 | 288 | 90 | 0.42 | 220 |

membranes increased with increase of Ca²⁺ content, and reached the highest value at $W_{Ca^{2+}} = 0.08$ mmol mg⁻¹, then decreased. It can be explained that the introduction of Ca²⁺ causes the increase of water content in the water-swollen membrane due to its hydrophilicity. However, Ca²⁺ crosslinked bridge favors improving structure and properties of the blend membranes.^{9,23}

Polymers Interpenetration Including Ca²⁺ Bridge

The experimental values of Ca²⁺ and Na⁺ content of the membranes AL, CCHAL-1, CCHAL-3, and CCHAL-5 determined by AAS are summarized in Table I. In our previous work, it has been indicated that during coagulation of alginic acid blend in 5 wt % CaCl₂ aqueous solution, an alginate-calcium complex, namely the membrane cross-linked with Ca²⁺, formed and the calcium in the membrane can not be substituted by other ions.⁷ Table II shows that the permeation flux of the blend membrane CCHAL-3 is much lower than that of the cellulose/alginic acid blend membranes RCA (8 : 2) and RCA (8 : 2)-Ca²⁺ crosslinked with

Ca²⁺, but the separation factor (α) for alcohol/water mixture is much higher than values of cellulose/alginic acid system. The Ca²⁺ crosslinking structure favors the selectivity and separation factors of membrane.^{9,23,27} From comparison of cellulose/alginic acid system^{7,23} to the CM-chitosan/alginic acid system, a dense architectural structure of the polymer chains exists in the CCHAL blend membranes, resulting from —NH₂ groups of CM-chitosan, and hindered the flow of the fluid. Moreover, when ratio of CM-chitosan/alginic acid was 1 : 1, the blend membrane (CCHAL-1) exhibited higher water resistivity and thermostability than the membranes of other blend components. It can be drawn that a polymers interpenetration caused by the electrostatic force between —NH₂ groups of CM-chitosan and —COOH groups of alginic acid occurred in the blend membranes of the CM-chitosan/alginic acid system.

CONCLUSIONS

The blend membranes were successfully prepared from O-carboxymethylated chitosan and alginate in

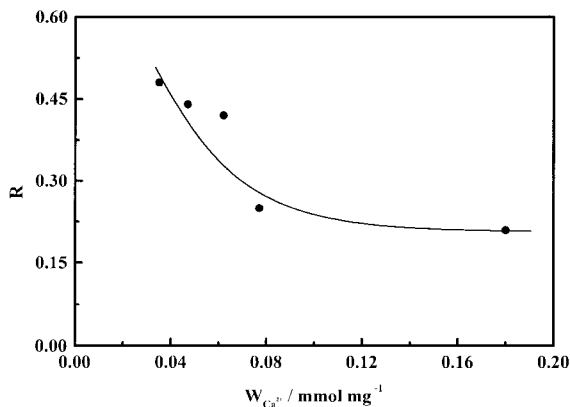


Figure 6 Dependence of water resistivity (*R*) of the membranes on Ca²⁺ content ($W_{Ca^{2+}}$).

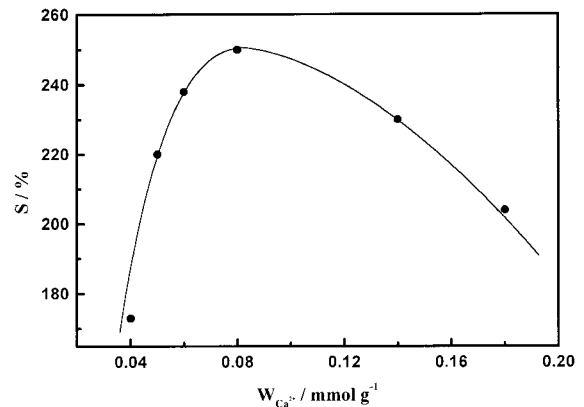


Figure 7 Dependence of *S* of the membranes on Ca²⁺ content ($W_{Ca^{2+}}$).

Table II Experimental Results of Permeation Flux (J) and Separation Factor (α) for Alcohol/Water Mixture on the Membranes

| Membrane | J ($\text{g h}^{-1} \text{m}^{-2}$) | α | Source |
|-----------------------------|---|----------|-----------|
| RCA(8 : 2) | 67 | 949 | 23 |
| RCA(8 : 2)-Ca ²⁺ | 68 | 1175 | 23 |
| CCHAL-3 | 8 | ∞ | This work |

aqueous solution, and they were miscible in the ratio from 1 : 1 to 1 : 5 for CM-chitosan/alginate, due to strong electrostatic force and hydrogen bonding between two polymers. The electrostatic interaction between —COOH groups of alginic acid and protonated —NH₂ groups of CM-chitosan in the blend membrane increased with the increase in CM-chitosan content until 50 wt %. The CM-chitosan in the blend membranes plays an important role in the dense architecture structure of the blend membranes. Therefore, the tensile strength (σ_b) in the wet state and thermostability of the blend membranes were markedly higher than that of nonblend and cellulose/alginate blend membrane,⁷ and the CCHAL-3 membrane have high separation factor in pervaporation for the alcohol/water mixture. The polymers interpenetration including Ca²⁺ crosslinked bridge occurred in the blend membranes, resulting in improving the structure and water resistivity. The blend membranes can be used in the wet state for various applications.

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REFERENCES

- Muzzarelli, R. in *Polymeric Biomaterials*; Dumitriu, S.; Ed., Marcel Dekker: New York, 1994.
- Hirano, S.; Seiono, H.; Akiyama, Y.; Nonaka, I. in *Progress in Biomedical Polymers*; Gebelein, C. G., Dunn, R. L., Eds.; Plenum Press: New York, 1990.
- Skjak-Braek, G.; Anthonsen, T.; Sandford, P. *Chitin and Chitosan*; Elsevier Press: New York, 1989.
- Zikakis, J. P. *Chitin, Chitosan and Related Enzymes*; Academic Press: New York, 1984.
- Shigemasa, Y.; Sashiwa, H.; Saimoto, H. *Polym J* 1986, 25, 993.
- Ibrahim, G.; Olle, L. WO Patent 96 02, 260, 1994.
- Zhang, L.; Zhou, D.; Wang, H.; Chen, S. *J Membrane Sci* 1997, 124, 195.
- Yeom, C. K.; Jegal, J. G.; Lee, K. H. *J Appl Polym Sci* 1996, 62, 1516.
- Huang, R. Y. M.; Pal, R.; Moon, G. Y. *J Membrane Sci* 1999, 160, 101.
- Sano, Y. *Carbohydr Polym* 1999, 38, 183.
- Nakamura, M. *Water Soluble Polymer*; Bessatsu Kagaku Kogyo, 1991.
- Sutton, A. *Nature* 1965, 216, 1005.
- Huguet, M. L.; Groboillot, A.; Neufeld, R. J.; Pancelet, D.; Dellacherie, E. *J Appl Polym Sci* 1994, 51, 1427.
- Wheatley, M. A.; Chang, M.; Park, E.; Languor, R. *J Appl Polym Sci* 1991, 43, 2123.
- Chancy, T.; Mooradian, D. L.; Rao, G. H. R. *J Appl Polym Sci* 1998, 70, 2143.
- Chen, R. H.; Tsaih, M. L. *J Appl Polym Sci* 1997, 66, 161.
- Yeom, L. K.; Lee, K. H. *J Appl Polym Sci* 1998, 67, 209.
- Zhang, L.; Yang, G.; Xiao, L. *J Membrane Sci* 1995, 103, 65.
- Muzzarelli, R. A. A. *Carbohydr Polym* 1988, 8, 1.
- Wu, C.; Wu, P.; Ma, X. *J Polym Sci Part B Polym Phys* 1996, 34, 221.
- Rabek, J. F. *Experimental Methods in Polymer Chemistry: X-ray Diffraction Analysis*; Wiley—Interscience: Chichester, 1980.
- Zhang, L.; Zhou, Q. *J Polym Sci Part B Polym. Phys* 1999, 37, 1623.
- Yang, G.; Zhang, L.; Peng, T.; Zhong, W. *J Membrane Sci* 2000, in press.
- Jiang, M.; Li, M.; Xiang, M.; Zhou, H. *Adv Polym Sci* 1999, 146, 121.
- Shukla, S.; Athalye, A. *J Appl Polym Sci* 1995, 57, 983.
- Gong, P.; Zhang, L.; Zhuang, L.; Lu, J. *J Appl Polym Sci* 1998, 68, 1321.
- Hirotsu, T.; Ichimura, K.; Mizoguchi, K.; Nakamura, E. *J Appl Polym Sci* 1988, 36, 1717.